III. "The Liquefaction and Solidification of Argon." By Dr. K. Olszewski, Professor of Chemistry in the University of Cracow. Communicated by Professor William Ramsay, F.R.S. Received January 28, 1895.

## (Abstract.)

Having been furnished, by Professor Ramsay's kindness, with a sample of the new gas, argon, I have carried out experiments on its behaviour at low temperatures and at high pressures, in order to contribute, at least in part, to the knowledge of the properties of this interesting body.

The argon with which I was supplied had been dried with phosphoric anhydride; its density was 19.9 (H = 1); and Professor Ramsay thought that at the outside it might contain 1 to 2 per cent. of nitrogen, although it showed no nitrogen spectrum when examined in a Pflücker's tube.

For the first two experiments I made use of a Cailletet's apparatus. As cooling agent I used liquid ethylene, boiling under diminished pressure.

In both the other experiments the argon was contained in a burette, closed at both ends with glass stop-cocks. By connecting the lower end of the burette with a mercury reservoir, the argon was transferred into a narrow glass tube fused at its lower end to the upper end of the burette, and in which the argon was liquefied, and its volume in the liquid state measured. In these two series of experiments liquid oxygen, boiling under atmospheric or under diminished pressure, was employed as a cooling agent. I made use of a hydrogen thermometer in all these experiments to measure low temperatures.

## Determination of the Critical Constants of Argon.

As soon as the temperature of the liquid ethylene had been lowered to -128°6, the argon easily condensed to a colourless liquid under a pressure of 38 atmospheres. On slowly raising the temperature of the ethylene, the meniscus of the liquid argon became less and less distinct, and finally vanished.

From seven determinations the critical pressure was found to be 50.6 atmospheres; the mean of the seven estimations of the critical temperature is  $-121^{\circ}$ .

At lower temperatures the following vapour-pressures were recorded:—

| Expt. | Temperature.           | Pressure.     | Expt.           | Temperature.           | Pressure.    |
|-------|------------------------|---------------|-----------------|------------------------|--------------|
| 8     | $-128^{\circ} \cdot 6$ | 38 · 0 atmos. | $1\overline{3}$ | $-134^{\circ} \cdot 4$ | 29 '8 atmos. |
| 9     | -129.6                 | 35.8 ,        | 14              | $-135 \cdot 1$         | 29.0 ,,      |
| 10    | $-129 \cdot 4$         | 35.8 ,,       | 15              | $-136 \cdot 2$         | 27 · 3 ,,    |
| 11    | <b>-</b> 129 · 3       | 35 ·8 ,,      | 16              | -138:3                 | 25 3 ,,      |
| 12    | -129.6                 | 35.8 ,,       | 17              | -139.1                 | 23.7 ,,      |

Determination of the Boiling and Freezing Points.

A calibrated tube, intended to receive the argon to be liquefied, and the hydrogen thermometer were immersed in boiling oxygen. On admitting argon, and diminishing the temperature of the liquid oxygen below  $-187^{\circ}$ , the liquefaction of the argon became manifest. When liquefaction had taken place, I carefully equalised the pressure of the argon with that of the atmosphere, and regulated the temperature, so that the state of balance was maintained for a long time. This process gives the boiling point of argon under atmospheric pressure. Four experiments gave the numbers  $-186^{\circ}.7$ ,  $-186^{\circ}.8$ ,  $-187^{\circ}.0$ , and  $-187^{\circ}.3$ . The mean is  $-186^{\circ}.9$ , which I consider to be the boiling point under atmospheric pressure (740.5 mm.).

The quantity of argon used for these experiments, reduced to normal temperature and pressure, was 99.5 c.c.; the quantity of liquid corresponding to that volume of gas was approximately 0.114 c.c. Hence the density of argon at its boiling point may be taken as approximately 1.5. This proves that the density of liquid argon at its boiling point (-187°) is much higher than that of oxygen, which I have found, under similar conditions, to be 1.124.

By lowering the temperature of the oxygen to  $-191^{\circ}$  by slow exhaustion, the argon froze to a crystalline mass, resembling ice; on further lowering temperature it became white and opaque. When the temperature was raised it melted; four observations which I made to determine its melting point gave the numbers:  $-189^{\circ}.0$ ,  $-190^{\circ}.6$ ,  $-189^{\circ}.6$ , and  $-189^{\circ}.4$ . The mean of these numbers is  $-189^{\circ}.6$ ; and this may be accepted as the melting point of argon.

In the following table I have given a comparison of physical constants, in which those of argon are compared with those of other so-called permanent gases. The data are from my previous work on the subject.

As can be seen from the foregoing table, argon belongs to the so-called "permanent" gases, and, as regards difficulty in liquefying it, it occupies the fourth place, viz., between carbon monoxide and oxygen. Its behaviour on liquefaction places it nearest to oxygen, but it differs entirely from oxygen in being solidifiable; as is well known, oxygen has not yet been made to assume a solid state.

The high density of argon rendered it probable that its liquefaction would take place at a higher temperature than that at which oxygen liquefies. Its unexpectedly low critical temperature and boiling point seem to have some relation to its simple molecular constitution.